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CRITICAL COMPARISON OF SOFT X-RAY FLUORESCENCE DETECTORS
FOR XAFS STUDIES IN THE 2 TO 4 KeV REGION

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Abstract

We report a performance comparison of fluorescence detectors for XAFS in the soft x-ray region. In particular this comparison was made under the practical constraints of an existing hard x-ray beamline (X-19A NSLS) double Si(111) crystal monochromator with a 10 mil beryllium exit window. A critical comparison of an energy dispersive proportional counter and an ionization chamber was performed above the sulfur K edge for a very dilute sample and a mixed element system. Third harmonic contributions and signal to background are discussed with the conclusion that an energy dispersive proportional counter provides superior results under our beamline constraints.

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Fluorescence Yield (FY) detection has been shown as a method of choice in measuring the x-ray absorption fine structure (XAFS) of dilute high atomic number (Z) atoms in solids and liquids.[1] However, the ability to determine local structure by means of XAFS is not limited to high Z atoms but has broad application in low Z and ultra low Z materials problems.[2,3] Although an appealing experimental tool for low Z materials characterization, soft x-ray fluorescence XAFS has technology challenges because of the attenuation of soft x-rays in most materials (including air!). In fact, we view this technical challenge as an opportunity for performing XAFS in situ studies of sulfur containing materials in air without the constraints of a vacuum environment.

Our experiments were performed at the National Synchrotron Light Source (NSLS) beamline X-19A[4] which utilizes a double flat crystal (Si(111)) NSLS boomerang-type[5] monochromator with ten mil (.010") beryllium exit window and no order sorting mirror in the system at present. Our experimental set up is shown schematically in Fig. 1 which includes an ionization chamber for measuring the incident intensity and a rotatable sample allowing the fluorescence signal to face our proportional counter or a standard Lytle ionization chamber.[6] The proportional counter used has a 5 mil beryllium entrance window 2 inches in diameter and is operated as a flow counter using P-10 gas (10% methane, 90% argon).[7] The counting electronics as shown in Fig. 1 indicates two single channel analyzers (SCA) which were used for simultaneous XAFS data collection in first and third order (described later in text).

At the low x-ray energies of interest for the sulfur K edge (2.472 keV) the 10 mil beryllium window acts as a high pass filter absorbing 92% of the 1st order beam and transmitting 90% of the third order beam (3×2.472 keV =

7.416 keV). This can be overcome somewhat by detuning the monochromator with an additional reduction in photon flux of 80% to 90%. This approach is highlighted in Fig. 2 which shows the detected energy spectrum (pulse height spectrum) from the proportional counter for a pure sulfur sample above and below the sulfur K edge at 50% monochromator detuning. Immediately evident is the enhancement of the sulfur K_{α} fluorescence line upon crossing the K edge. However, even at 50% monochromator detuning there is a substantial third order elastically scattered peak. By utilizing a single channel analyzer we can easily set a window to collect only the signal from the sulfur K_{α} line discriminating totally the third order elastic scattering contribution. For the case of the ionization chamber, the situation is quite poor in comparison because of the lack of energy discrimination. In fact the third harmonic contribution to the total ion current collected is weighted three times that of the sulfur K_{α} first harmonic because each third harmonic photon creates three times as many electron ion pairs as the first harmonic. This has the unfortunate effect of increasing the background measured by the ionization chamber and forcing one to detune the monochromator even further in order to reduce the background to an acceptable level.

As an XAFS comparison we used a low sulfur concentration sample (<.01% sulfur) of crude oil in air using both detectors described above, the resulting near edge spectra are shown in Fig. 3. Both detection methods were able to collect the required data, however the signal to noise of the proportional counter data is at least 10 times better which is critical in the case of obtaining good XAFS data capable of reliable data reduction using the standard fourier transform methods. It is also instructive to note that 80% detuning was required in order to generate reasonable signal to background for the ionization chamber detector. On the other hand the 50% detuning for the proportional counter data merely reflects a need to reduce the overall intensity to avoid excessive dead time problems.

Our final XAFS comparison was made for a 5% cobalt sulfide sample as an example of a mixed element system. The proportional counter data from this sample was taken using two simultaneous single channel analyzers; one windowed on the sulfur K_{α} line (2.307 keV) excited by the first harmonic and a second SCA windowed on the cobalt K_{α} line (6.930 keV) excited by the third harmonic. The resulting near edge spectra are shown in Fig. 4, which shows no hint of any cobalt features in the 1st order sulfur K edge spectrum. Also shown is the simultaneous cobalt K edge spectrum from the third harmonic. In contrast, the ionization chamber data suffers from a cobalt feature in the sulfur K edge data because of third harmonic contamination. As a result the ionization chamber is not well suited to this type of mixed element sample. The only recourse for the ionization chamber method is further detuning or the use of a low pass filter in front of the detector, both of which reduce the intensity too much. As a matter of practical experience, the cobalt feature could be reduced by such methods, but it never disappears.

In conclusion, we have shown that an energy dispersive proportional counter has important advantages for low Z fluorescence yield XAFS measurements. In particular, we have shown that for a beamline with a beryllium exit window operating in air energy dispersive detection is essential to obtain good signal to background. Because the first and third harmonic are widely separated in energy, a proportional counter is an ideal solution in terms of construction ease and low cost as compared to a solid state detector; although this may have advantages in mixed element systems with closely spaced fluorescence lines.

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Figure Captions

- Fig. 1. A schematic diagram of the experimental setup for comparing fluorescence detectors. The sample is rotatable allowing it to face a proportional counter or an ionization chamber.
- Fig. 2. Pulse height spectra above and below the sulfur K edge for the X-ray fluorescence yield of pure sulfur with the monochromator 50% detuned.
- Fig. 3. Sulfur near edge x-ray absorption of crude oil (<.01% sulfur) in air. Upper curve utilizes the proportional counter described in the text and the lower curve utilizes an ionization chamber.
- Fig. 4. X-ray absorption spectra of 5% cobalt sulfide in boron nitride. The proportional counter spectra were taken simultaneously in first and third order. The ionization chamber spectrum shows a cobalt feature due to third order contamination.

Fig 1

Fig. 2

Fig 3

Fig. 4